

PATENT SPECIFICATION

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(54) PROCESS FOR PRODUCING VINYL CHLORIDE

(71) We, THE BRITISH PETRO-
 LEUM COMPANY LIMITED, of
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 EC2Y 9BU, a British company, do hereby
 declare the invention, for which we pray
 that a patent may be granted to us, and the
 method by which it is to be performed, to
 be particularly described in and by the
 following statement:—

The present invention relates to the
 oxychlorination of ethane.

The chlorination of hydrocarbons with
 hydrogen chloride and oxygen in the
 vapour phase at elevated temperature in
 the presence, as catalyst, of cupric chloride
 deposited on support material is known. It
 is an object of the present invention to
 provide an improved catalyst for such an
 oxychlorination reaction.

Accordingly, the present invention is a
 process for the production of vinyl chloride
 monomer comprising contacting at
 elevated temperature a reaction feed
 containing ethane, hydrogen chloride and
 molecular oxygen in the vapour phase with a
 catalyst comprising a copper halide, a
 halide of an alkali metal or an alkaline earth
 metal and a rare earth metal compound as
 hereinafter defined deposited on activated
 alumina, said catalyst composition
 containing above 5% by weight of the alkali
 metal or alkaline earth metal in a free or a
 combined form.

The copper halide in the catalyst
 composition may be introduced either in
 the form of the halide as such or in the form
 of a copper compound, e.g. copper oxide or
 copper nitrate which under the reaction
 conditions would be converted to the
 corresponding halide. It is however,
 preferable to use copper chlorides.
 Whichever method is used to introduce
 copper halide, the catalyst including the
 support preferably contains between 5 and
 10% by weight of copper.

The alkali metal or alkaline earth metal
 halide in the catalyst acts as a promoter. The

proportion of alkali metal or alkaline earth
 metal halide employed should be such that
 the ultimate catalyst composition including
 the support contains above 5% by weight of
 the alkali metal or alkaline earth metal. The
 alkali metals may be selected from sodium,
 potassium, lithium and caesium; the
 alkaline earth metal is suitably magnesium
 or calcium. The catalyst may contain more
 than one alkali and/or alkaline earth metal
 in combined form. The preferred alkali
 metal halide is potassium chloride. The
 surprising feature of the present invention is
 that by increasing the amount of alkali or
 alkaline earth metal halide, the yields of
 vinyl chloride and ethylene based on ethane
 fed were improved considerably.

The third component in the catalyst
 composition of the present invention is a
 "rare earth metal" compound. By the term
 "rare earth metal" is meant here and
 throughout the specification the metals of
 atomic numbers between 57 and 71
 (inclusive) e.g. cerium, lanthanum and
 neodymium. It is preferable to use
 technical cerium chloride derived from a
 mixture of lanthanons found in monazite
 which has the following approximate
 composition: La₂O₃, 23%, CeO₂, 45%, Pr₆O₁₁,
 6%, Nd₂O₃, 18%, Sm₂O₃, 3% and other
 lanthanon oxides 5%.

The function of these rare earth metal
 compounds in the catalyst composition is to
 reduce the volatility of the copper content
 of the catalyst thus increasing the activity of
 the catalyst markedly. The proportion of
 the rare earth metal compound employed is
 suitably such as to provide from 0.2 to 10%
 by weight of the total catalyst composition
 including the support.

The alumina support may be activated by
 heating for at least 2 hours at a temperature
 between 500°C and 1,400°C, preferably
 between 700°C and 1,200°C. This
 activation is suitably carried out before the
 deposition of the catalyst components.
 Such heat treatment reduces the amount of

carbon dioxide present in the reaction product and the yield of the desired chlorinated hydrocarbon is substantially increased.

- 5 The support may be impregnated with the catalyst components directly with a solution of the copper compound, alkali metal halides and the rare earth compound. Alternatively, the copper compound, alkali
- 10 metal halide and the rare earth metal compound may be impregnated on the support successively in any order.

- The ethane may be fed to the reaction feed as any suitable ethane containing mixture, for example the ethane/ethylene mixtures available from technical C₂ containing gas streams. Since one of the by-products of the reaction for the present invention is ethylene, this may be recycled and mixed with fresh feeds of ethane. The relative proportions of the reactant in the feed may correspond substantially with the stoichiometric requirements of the reaction being carried out. In operation, however, it
- 25 may be desirable to employ either an excess of the ethane and/or of oxygen to obtain maximum conversion of the hydrogen chloride to product. The oxygen in the feed may be provided by any suitable molecular oxygen containing gas such as air, although it would be appreciated that recovery and recycle of reactants is facilitated by use of pure undiluted molecular oxygen. Diluents such as nitrogen
- 35 or steam may also be present.

- Reaction temperatures may suitably range from 300°C to 550°C. The contact time would vary with the reaction temperature and may range between 0.1 and 20 seconds, preferably between 2 and 10 seconds.
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- The hydrogen chloride may be provided from any suitable source, for example as waste hydrogen chloride from the pyrolysis of 1,2-dichloroethane to produce vinyl chloride. The hydrogen chloride may also be diluted or partially be replaced by chlorine.
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- Products of the process of the present invention include vinyl chloride, ethylene, ethyl chloride and 1,1- and 1,2-dichloroethanes. The latter two substances may be further pyrolysed to vinyl chloride and hydrogen chloride. This hydrogen chloride may be recovered and recycled to the oxychlorination reactor as indicated above. Ethylene, ethyl chloride and the aforementioned dichloroethanes, may also be recycled to the oxychlorination reactor to give additional vinyl chloride.
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The invention is further illustrated with reference to the following Examples:

Example 1

The catalyst was prepared by

impregnating alumina (50 g Alcoa (Regd. Trade Mark) F.1 grade 4—10 mesh granules), which had been heat-treated at 1050°C for 24 hours, with an aqueous solution (40 ml) containing cupric chloride hydrate (3.43 g), potassium chloride (7.5 g) and technical grade cerium chloride hydrate (5.0 g). The excess water was evaporated off and the residue dried at 150°C for 16 hours. The catalyst thus contained normally 6.2% potassium and 2% copper expressed on a water free basis. A gaseous mixture containing ethane (7% v/v), hydrogen chloride (7% v/v), air (32.9% v/v) and nitrogen (53.1% v/v) was passed over the catalyst at 530°C. The contact time was 4 seconds. Of the ethane fed, 40.1% was converted to vinyl chloride, 38.3% to ethylene and 4.7% to carbon oxides. The overall conversion of ethane was 98.1%, and 77% of the hydrogen chloride was consumed.

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Example 2

The catalyst was prepared by impregnating alumina (50 g Alcoa (Regd. Trade Mark) F1 grade 4—10 mesh granules), which had been heat-treated at 1050°C for 24 hours, with an aqueous solution (45 ml) containing cupric chloride hydrate (6.86 g), potassium chloride (9.0 g) and technical grade cerium chloride hydrate (10.0 g). The excess water was evaporated off and the residue dried at 150°C for 16 hours. The catalyst thus contained nominally 6.6% potassium and 3.6% copper, expressed on a water-free basis.

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A gaseous mixture containing ethane (7% v/v), hydrogen chloride (6.8% v/v), air (33.4% v/v) and nitrogen (52.8% v/v) was passed over the catalyst at 530°C. The contact time was 4 seconds. Of the ethane fed, 43.5% was converted to vinyl chloride, 39.5% to ethylene and 4.2% to carbon oxides, the conversion of ethane was 96.5%, whilst 77% of the hydrogen chloride was consumed.

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Example 3

The catalyst was prepared as described in Example 2, except that cupric chloride hydrate (4.19 g), potassium chloride (13.5 g) and technical grade cerium chloride hydrate (6.23 g) were used. The catalyst nominally contained 10% potassium and 2.2% copper, expressed on a water free basis.

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A gaseous mixture containing ethane (6.9% v/v), hydrogen chloride (6.9% v/v), air (33.6%) and nitrogen (52.6%) was passed over the catalyst at 530°C, 4 seconds contact time. Of the ethane fed, 42.5% was converted to vinyl chloride, 36% to

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ethylene and 4.4% to carbon oxides. The ethane conversion was 99%.

Example 4

The catalyst was prepared as described in Example 2, except that cupric chloride hydrate (5.75 g), potassium chloride (37.1 g) and technical grade cerium chloride (8.55 g) were used. The catalyst nominally contained 20% potassium and 2.2% copper, expressed on a water free basis.

A gaseous feed containing ethane (7.2% v/v), hydrogen chloride (7.1% v/v), air (33.2%) and nitrogen (52.5%) was passed over the catalyst at 530°C, 4 seconds contact time. Of the ethane fed, 39.5% was converted into vinyl chloride, 39% to ethylene and 3.5% to carbon oxides. The ethane conversion was 98.8%.

Example 5

The catalyst was prepared as described in Example 2, except that cupric chloride hydrate (3.43 g), caesium chloride (10.1 g) and technical grade cerium chloride hydrate (5.0 g) were used. The catalyst nominally contained 12.1% caesium and 1.93% copper, expressed on a water free basis.

A gaseous mixture containing ethane (7.1% v/v), hydrogen chloride (7% v/v), air (33.7% v/v) and nitrogen (52.2% v/v) was passed over the catalyst at 530°C, 4 seconds contact time. Of the ethane fed, 37.4% was converted into vinyl chloride, 43% to ethylene and 4.8% to carbon oxides. The conversion of ethane was 95%.

WHAT WE CLAIM IS:—

1. A process for the production of vinyl chloride monomer comprising contacting at elevated temperature a reaction feed containing ethane, hydrogen chloride and molecular oxygen in the vapour phase with a catalyst composition comprising a copper halide, a halide of an alkali or alkaline earth metal and a rare earth metal compound as hereinbefore defined deposited on activated alumina, said catalyst composition containing above 5% by weight of the alkali or alkaline earth metal in a free or combined form.

2. A process according to claim 1

wherein the copper halide in the catalyst composition is copper chloride.

3. A process according to claim 1 wherein the alkali metal is selected from sodium, potassium, lithium and caesium.

4. A process according to claim 1 wherein the alkaline earth metal is calcium or magnesium.

5. A process according to any one of the preceding claims wherein the halide of the alkali or alkaline earth metal is a chloride.

6. A process according to any one of the preceding claims wherein the catalyst composition contains between 0.2 and 10% by weight of the rare earth metal compound.

7. A process according to any one of the preceding claims wherein the alumina is activated by heating for at least 2 hours between 500°C and 1,400°C prior to the deposition of the other catalyst components.

8. A process according to any one of the preceding claims wherein the ethane is fed to the reaction feed as a mixture thereof with ethylene.

9. A process according to any one of the preceding claims wherein the oxygen feed is diluted with steam or nitrogen.

10. A process according to any one of the preceding claims wherein hydrogen chloride is partially replaced by chlorine.

11. A process according to any one of the preceding claims wherein the reaction feed is contacted with the catalyst composition at a temperature in the range of 300°—550°C, for between 0.1 and 20 seconds.

12. A process according to claim 11 wherein the reaction feed is contacted with the catalyst for between 2 and 10 seconds.

13. A process for producing vinyl chloride monomer according to claim 1 as hereinbefore described with reference to the Examples.

14. Vinyl chloride monomer whenever produced by a process according to any one of the preceding claims.

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